

DESIGN AND OPERATION OF AN ELECTROCHEMICAL METHANOL CONCENTRATION SENSOR FOR DIRECT METHANOL FUEL CELL SYSTEMS

S. R. Narayanan*, T. I. Valdez, and W. Chun

Jet Propulsion Laboratory, California Institute of Technology

4800 Oak Grove Drive, Pasadena, CA 91109

Abstract

The design and operation of a methanol concentration sensor suitable for use with direct methanol fuel cells is described. The sensing principle is based on the measurement of the diffusion-controlled current for the electro-oxidation of methanol in a polymer electrolyte membrane cell at a platinum-ruthenium electrode. The device construction and properties are described. The sensor has been integrated with an automatic fuel feed system, and has been operated for several tens of hours. The results demonstrate that the sensor is robust and sensitive to meet the demands of concentration sensing and control in direct methanol fuel cell systems.

*Electrochemical Society Active Member

DESIGN AND OPERATION OF AN ELECTROCHEMICAL METHANOL CONCENTRATION SENSOR FOR DIRECT METHANOL FUEL CELL SYSTEMS

S. R. Narayanan, T. I. Valdez, and W. Chun

Jet Propulsion Laboratory, California Institute of Technology

4800 Oak Grove Drive, Pasadena, CA 91109

Introduction

Direct methanol fuel cells based on the direct oxidation of an aqueous liquid solution of methanol and a polymer electrolyte membrane have been the subject of considerable research during the last ten years [1-7]. As a result, significant improvements in power density, efficiency and life have been reported. Performance realized in cells, stacks and systems show that this technology is a promising power source for a wide range of portable applications [5,7] .

A 50-watt direct methanol fuel cell system has been demonstrated [2, 4], and the development of a 150-Watt packaged power source is being pursued currently at the Jet Propulsion Laboratory for defense applications. The layout for the direct methanol fuel cell system is shown in Fig. 1. In this system configuration, a dilute solution of methanol of a specified concentration enters the stack. After passage through the stack methanol is consumed in the production of electricity and the concentration of methanol in the

solution decreases. Pure methanol is added to the solution loop to maintain the required concentration. The concentration of methanol in the fuel circulation loop is an important operating parameter in that it determines the electrical performance and efficiency of the direct methanol fuel cell system [1,2,6,8]. While high methanol concentration allows the attainment of higher power densities, this also results in increased fuel loss by crossover and low fuel cell efficiency. The power density and the rate of fuel crossover at a chosen cell voltage are strong functions of the operating temperature. Hence, the methanol concentration specifications for attaining the highest efficiency vary with the operating stack temperature. Also the start-up procedure, transient performance requirements, idling mode and steady-state operation could require the methanol concentration to be specified differently [4,5]. In short, the practical operation of direct methanol fuel cell systems requires accurate monitoring and control of methanol concentration.

Based on our experience with direct methanol fuel cell systems, a viable methanol concentration sensor should have a sensitivity of about ± 0.02 M over the range of 0.1-2M, with a response time of less than a second, although in general such specifications would be highly dependent on the mode of operation and the application. Such a sensor must also be robust and amenable to miniaturization. To this end, several methods of measurement of methanol concentration were considered. Among these were measurement of physical properties such as density, refractometry and ultra-violet light absorptivity. None of these methods satisfied all the desired criteria. The present paper reports on the principle and demonstration of an in-house developed electrochemical

sensor that meets the above-said sensor requirements. A recent report [9] on an electrochemical methanol concentration sensor addresses this need in a similar way.

Electrochemical Sensing Principle

The electro-oxidation of methanol to carbon dioxide on platinum-ruthenium catalysts [1,2] is the basis of the operation of the methanol concentration sensor. Figure 2 shows the polarization characteristics of the platinum-ruthenium anode in a direct methanol fuel cell fabricated with Nafion® 117 as the polymer electrolyte membrane. These polarization curves show that at potentials above 0.45 V the kinetics of electro-oxidation of methanol is significantly controlled by mass transfer of methanol to the electrode/solution interface surface. Thus the oxidation current at high anode potentials is determined by the bulk concentration, the mass-transfer coefficient, the diffusion layer thickness and temperature. The dependence of the oxidation current on bulk concentration at 0.55 V is shown in Fig. 3. This data suggests that the oxidation current sustained at the methanol electrode under mass-transport-limited conditions could be used to devise a sensor for methanol concentration.

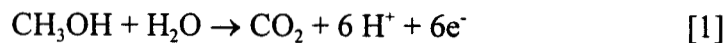
Experimental Design of Sensor

In implementing the principle described above, the diffusion-controlled oxidation current at the methanol electrode must be measured at set values of anode potential in the range 0.45-0.65 V. While implementing a reference electrode to maintain the potential

of the methanol electrode is straightforward for liquid electrolytes, the polymer electrolyte presents practical difficulties and uncertainties. Thus a reference electrode was not considered. Instead a relatively non-polarizing counter electrode sustaining a fast electrochemical reaction such as hydrogen evolution could function as a pseudo-reference within limits. The construction of the sensor is shown in Fig.4. The sensing element consists of Nafion® 117 membrane catalyzed with unsupported platinum-ruthenium catalyst on anode side and platinum black on the cathode side. In-house prepared platinum-ruthenium catalyst (50/50 atom %) and commercial “fuel cell grade” platinum black was used. The catalyst loading was in the range of 2-4 mg/cm². The backing layers were prepared from wet-proofed Toray paper. The membrane and electrodes were hot pressed to obtain a membrane-electrode assembly. The active electrode area was about 0.3-0.5 cm². The sensor element was held between two graphite plates that served as current collectors. The graphite plates also exposed a defined circular area of the electrode. The glass fixture surrounding the sensor element allowed the circulation of an aqueous methanol feed past both sides of the membrane electrode assembly. This particular arrangement renders the sensor highly suitable for in-line or “dip-type” integration into a fuel circulation loop. The overall device size is in about 2 cm³ and the construction of the sensor does not present significant challenges to further miniaturization, if necessary.

During sensor operation, the terminal voltage between the sensor electrodes was held at a specified value in the range of 0.45-0.65 V with the platinum-ruthenium electrode being the positive electrode. Under these conditions the platinum-ruthenium electrode sustained the mass transfer controlled electro-oxidation of methanol and the

platinum electrode sustained the evolution of hydrogen. The electrochemical reactions at the two electrodes are shown below:



The transport of methanol to the Pt-Ru/Nafion interface occurs through the backing layers, the electrocatalyst layers, and the membrane. The platinum electrode sustains the hydrogen evolution reaction, exhibits a stable electrode potential, and functions as a pseudo-reference electrode. During operation the sensor is placed in the circulating stream of the methanol solution and the solution moves first past the anode of the sensor and then the cathode. Such an arrangement will ensure that the hydrogen produced at the cathode of the sensor will not contribute to any oxidation current. The temperature of the methanol solution in the sensor is measured so that the calculated concentration can be compensated for the dependence of mass-transport-limited current on temperature.

Results of Sensor Operation

A practical sensor is qualified by sensitivity, response time, robustness, and power demand. Results relating to these properties are now addressed. Figure 5 shows the dependence of the measured sensor current at various temperatures, terminal voltages, and concentration. The sensitivity can be expressed as the observable change in

oxidation current density per molar change in concentration, and this is in the range of 100-500 mA cm⁻² M⁻¹ at 0.65 V over a wide temperature range. The rate of electro-oxidation increases with potential and temperature and thus results in increased sensitivity. The dependence of oxidation current on temperature and the difference in sensitivity observed at different temperatures requires that temperature compensation be built into the calculation of concentration. The measured changes in current density are significant enough to allow monitoring of changes as small as 0.01M. Miniaturization of the sensor can be achieved without loss of sensitivity, as the actual value of current is itself significant in magnitude for measurement purposes. Based on results similar to that shown in Fig. 5 a mathematical correlation between temperature, concentration and oxidation current was established for concentration monitoring.

The sensor was operated as part of a direct methanol system under test for several tens of hours with no noticeable degradation. At a terminal voltage of 0.65V the anode is well below the range where the stability of Pt-Ru catalyst is of any concern. In fact platinum-ruthenium catalysts have not shown any noticeable degradation in fuel cells tested for over several thousands of hours of operation [10]. Since materials used in the sensor are same as that present in the fuel cell, the chemical stability is expected to be comparable to the fuel cell itself. It will be important to maintain the membrane-electrode element of the sensor in a hydrated state during non-operation and storage to prevent damage to the membrane-electrode element and loss of calibration, just as in the case of the fuel cell. The present design of the sensor relies on the carbon paper structures and the membrane to function as the mass transfer barrier. Although no degradation was noticeable over a three-month period, the carbon paper could be

substituted with carbon cloth or sintered-metal structures to provide extended long-term robustness.

The response times for the sensor are governed by time constants for mass transfer to the electrode/membrane interface. The order of magnitude estimate of this time constant, t , can be obtained from Einstein's relationship, $t = l^2 / 2D$ where l is the thickness of the diffusion layer and D is an apparent diffusion coefficient for methanol through the various structures in the sensor element. The estimated time constant for typical values of the parameters is about 100 milliseconds. By modifying the thickness of the diffusion barriers and the diffusivity, even lower time constants can be achieved. Experimental studies of steady state sensor operation suggest a response time not greater than 0.2 s. This time constant is quite acceptable for control of concentration in fuel cell systems.

Direct methanol fuel cell system operation with methanol sensor

An automated feedback system for concentration measurement and control based on the sensor and a fuel injection device was integrated as part of a demonstration of a direct methanol system similar to that shown in Fig.1. The terminal voltage of the sensor was held at 0.65 V. The current through the cell was monitored and the temperature-compensated molarity was calculated using the correlation developed earlier. This molarity value became the input to a decision making loop that controlled the methanol feed pump. The measurement and control was carried out with a PC in Labview™ environment. Figure 6 shows the results of a typical experiment to demonstrate concentration control. At first to demonstrate the concentration monitoring capability of

the sensor, a load of 14 A was impressed on the fuel cell stack. The feed of pure methanol was deliberately turned off. This resulted in a rapid decline of concentration in the fuel loop. Figure 6 shows that this decline in concentration as tracked by the sensor. This also demonstrates that the measurement sensitivity of ± 0.01 M is achievable. Then, after an elapse of 35 minutes the pulse feed of pure methanol was turned on and the concentration rose in the loop. At this time there was no load impressed on the fuel cell system. Spikes in the lower portion of the figure indicate the pulse feed events. Subsequently, after reaching 0.5 M the load on the stack was maintained at 10 A and at this time the concentration sensor and the pulse feed were coupled in a feedback loop. The results show that the concentration of 0.5 M could be maintained over a period of 30 minutes by interactively coupling the sensor and the pulse feed. In another experiment a 5-cell stack with an electrode area of 80 cm^2 was continuously operated at a current density of 100 mA cm^{-2} (equivalent to a stack current of 8 A) for over 70 hours with a circulating stream of 0.5 M methanol. During this test approximately a liter of methanol was injected into the fuel stream and results shown in Fig. 7 demonstrate that the concentration sensor along with the pulse feed of methanol could maintain the concentration at 0.49 ± 0.02 M during an entire 70 hour test. Currently the sensor is being integrated into a 150-Watt DMFC power system.

Conclusions

The results described above show that a practical methanol concentration sensor based on the mass-transfer-limited electro-oxidation of aqueous methanol solutions can be constructed and implemented. The sensor has sensitivity, robustness and time response characteristics required for control and monitoring of methanol concentration in direct methanol fuel cell systems.

Acknowledgment

This work was performed at the Jet Propulsion Laboratory, California Institute of Technology, under the sponsorship of the Defense Advanced Research Projects Agency and the U. S. Army Research Office/ University of Minnesota under a contract with the National Aeronautics and Space Agency.

References

1. S.Surampudi, S. R. Narayanan, E. Vamos, H. Frank and G.Halpert, A. Laconti, J. Kosek, G. K. Surya Prakash, and G. A. Olah, *J. Power Sources*, **47**, 377 (1994).
2. S. R. Narayanan, A. Kindler, B. Jeffries-Nakamura, W. Chun, H. Frank, M.Smart , S. Surampudi and G. Halpert, in "*Proton Conducting Fuel Cells I* ", S. Gottesfeld, G. Halpert and A. Landgrebe, Editors, PV 95-23, p.261 The Electrochemical Society, Proceedings Series, Pennington, NJ (1995).
3. X. Ren, M. S. Wilson, and S. Gottesfeld, *J. Electrochem. Soc.*, **143** L12 (1996)
4. S. R. Narayanan, T. Valdez, N. Rohatgi, J. Christiansen, W.Chun, G. Voecks and G. Halpert, Proceedings of the 38th Power Sources Conference, p. 461, Cherry Hill, NJ, June 1998.
5. S. R. Narayanan, T. I. Valdez, N. Rohatgi, W.Chun and G. Halpert, *1998 Fuel Cell Seminar*, Abstracts, p. 707, Palm Springs, CA November 1998.
6. T. I. Valdez and S. R. Narayanan, "*Proton Conducting Fuel Cells II* ", S. Gottesfeld, and T. Fuller, Editors, PV 98-27, p. 380 The Electrochemical Society, Proceedings Series, Pennington, NJ (1998).
7. P. Zelenay, S.C. Thomas and S.Gottesfeld "*Proton Conducting Fuel Cells II* ", S. Gottesfeld, and T. Fuller, Editors, PV 98-27, p. 300 The Electrochemical Society, Proceedings Series, Pennington (1998)
8. S. R. Narayanan, A. Kindler, B. Jeffries-Nakamura, W. Chun, and G. Halpert, in "*Proton Conducting Fuel Cells I* ", S. Gottesfeld, G. Halpert and A. Landgrebe,

Editors, PV 95-23, p.278 The Electrochemical Society, Proceedings Series, Pennington, NJ (1995).

9. S. A. Calabrese Barton, B.L.Murach, T. F. Fuller and A. C. West, J. Electrochem. Soc., **145** 3783 (1998)
10. J. A. Kosek, C. C. Cropley, M. Hamdam and A. Shramko, 1998 Fuel Cell Seminar Abstracts p. 693, Palm Springs, CA, November 1998.

Figure captions

Figure 1. Schematic of a direct methanol fuel cell system showing location of methanol concentration sensor in the fuel circulation loop.

Figure 2. Polarization curves for methanol oxidation at a Pt-Ru/Nafion interface obtained from polymer-electrolyte membrane direct methanol fuel cell operating at 90°C with various concentrations of methanol.

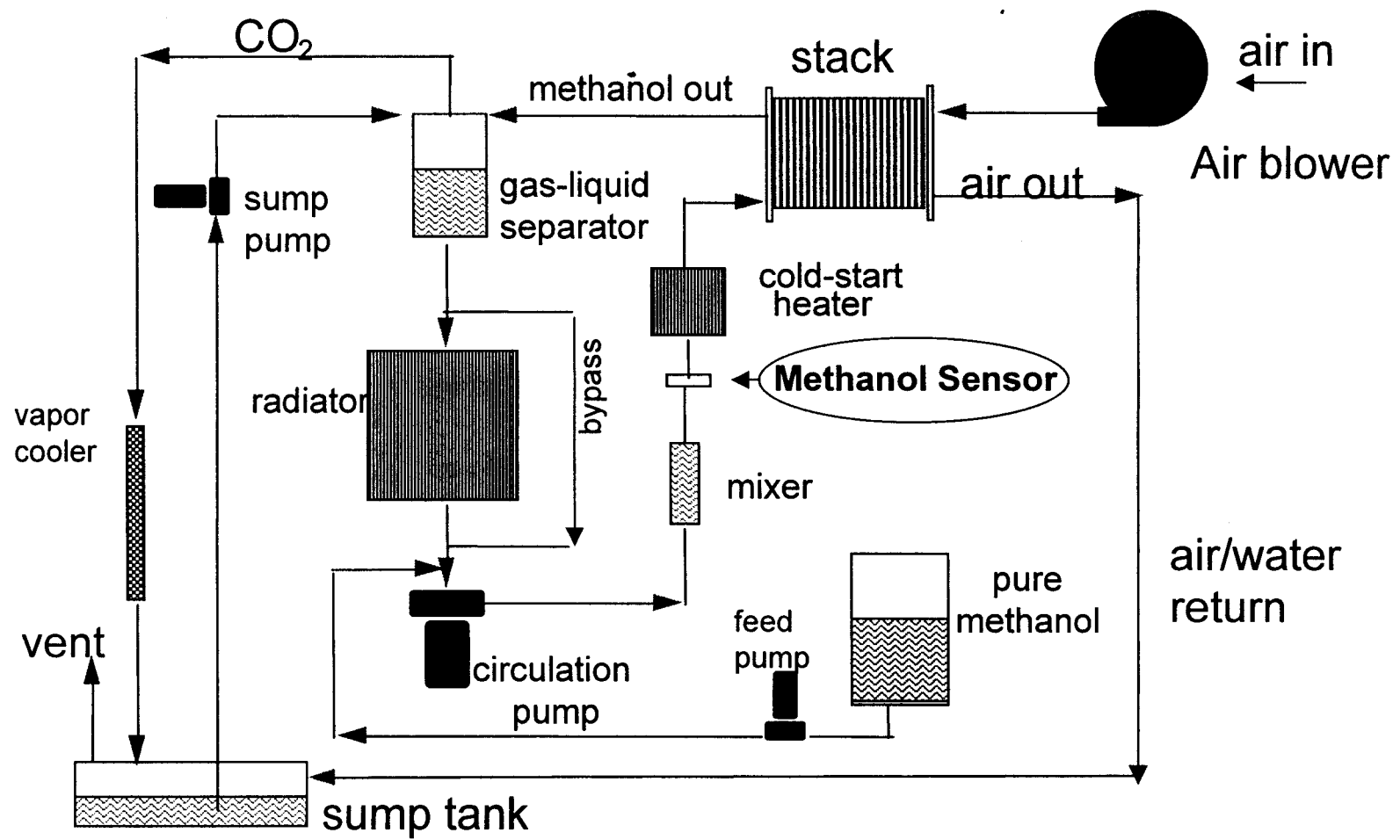
Figure 3. Dependence of diffusion controlled methanol oxidation current on concentration at 0.55V at 90°C.

Figure 4. Details of construction of the methanol sensor.

Figure 5. Dependence of the measured sensor current on the concentration of methanol at various temperatures and cell voltages.

Figure 6. Results of concentration monitoring and control during system operation at 60°C and 0.5 M methanol. Stack current, stack voltage and pulsed methanol feed are shown along with methanol concentration changes.

Figure 7. Results of concentration monitoring and control during 5-cell stack operation at 8 A at 60 °C. Stack Voltage and Fuel loop molarity is indicated.



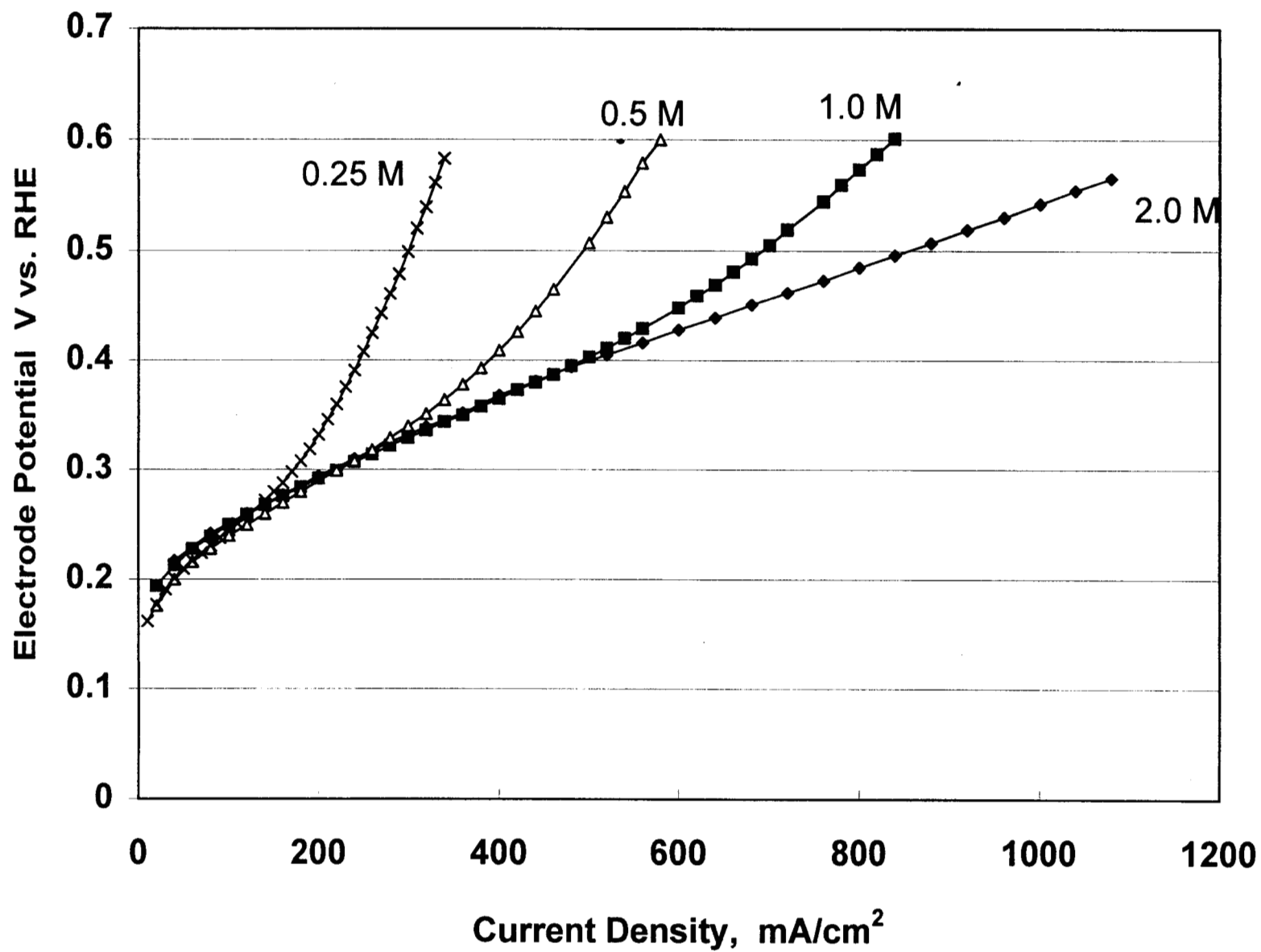


Fig. 2

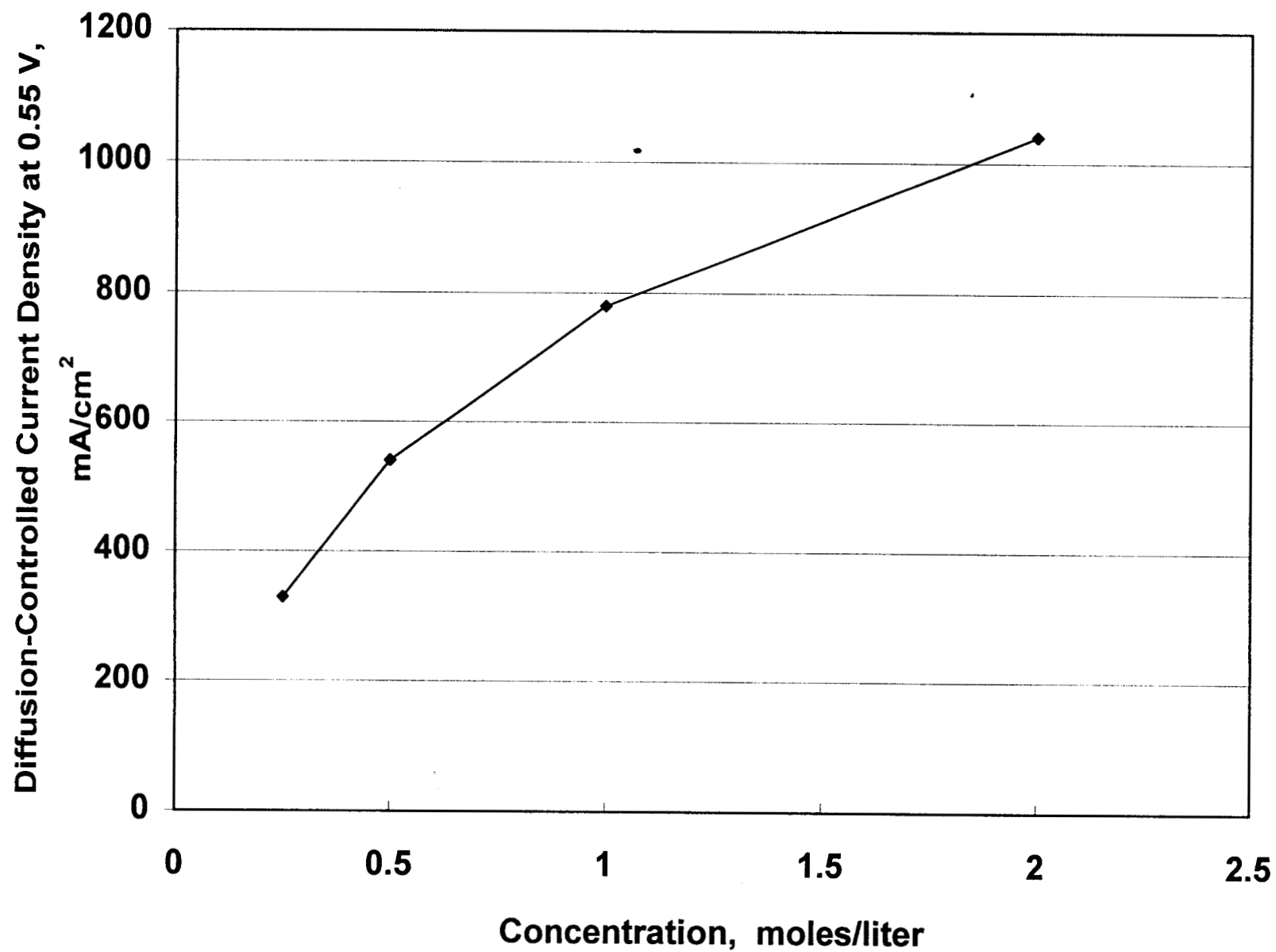
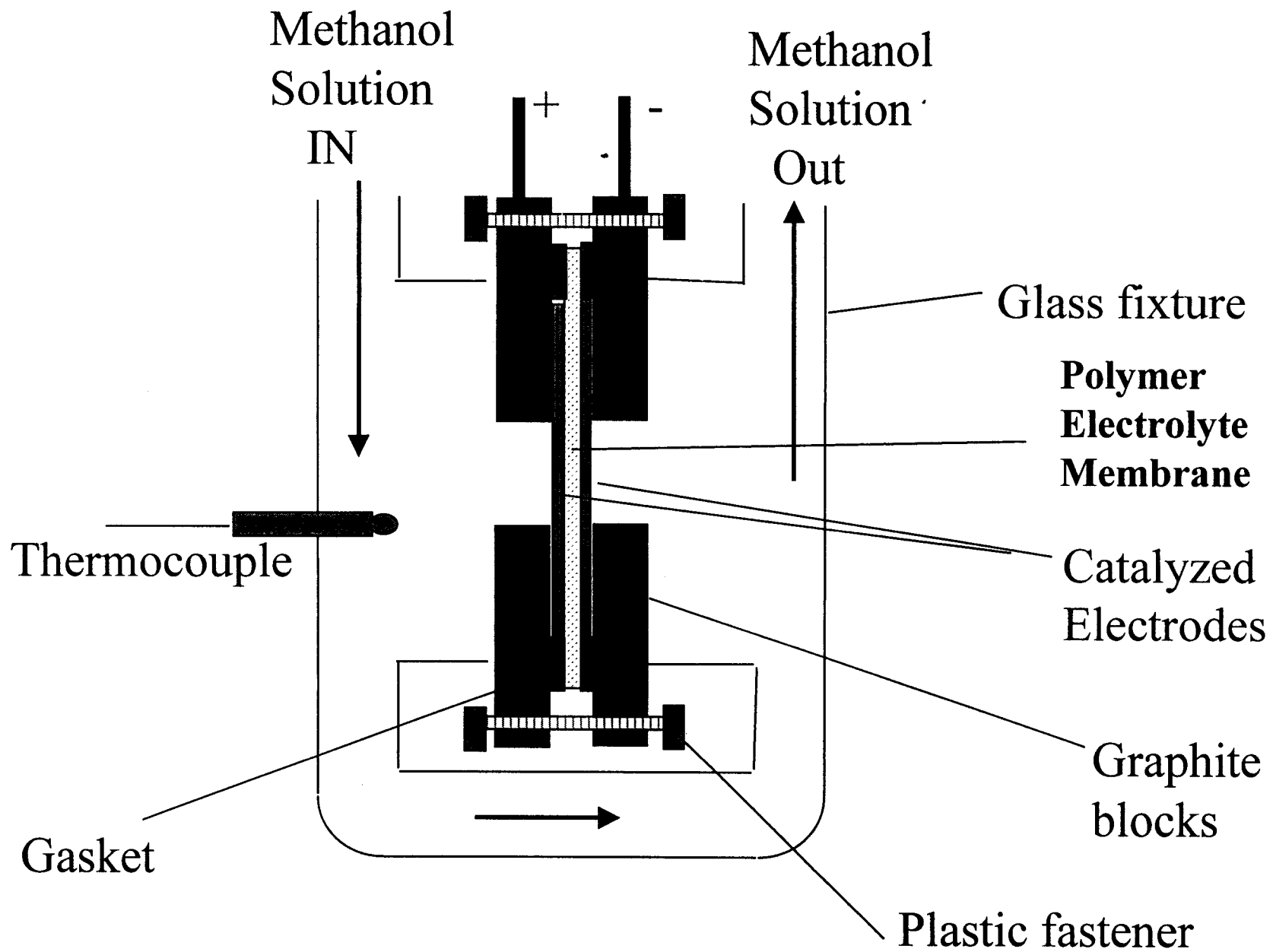
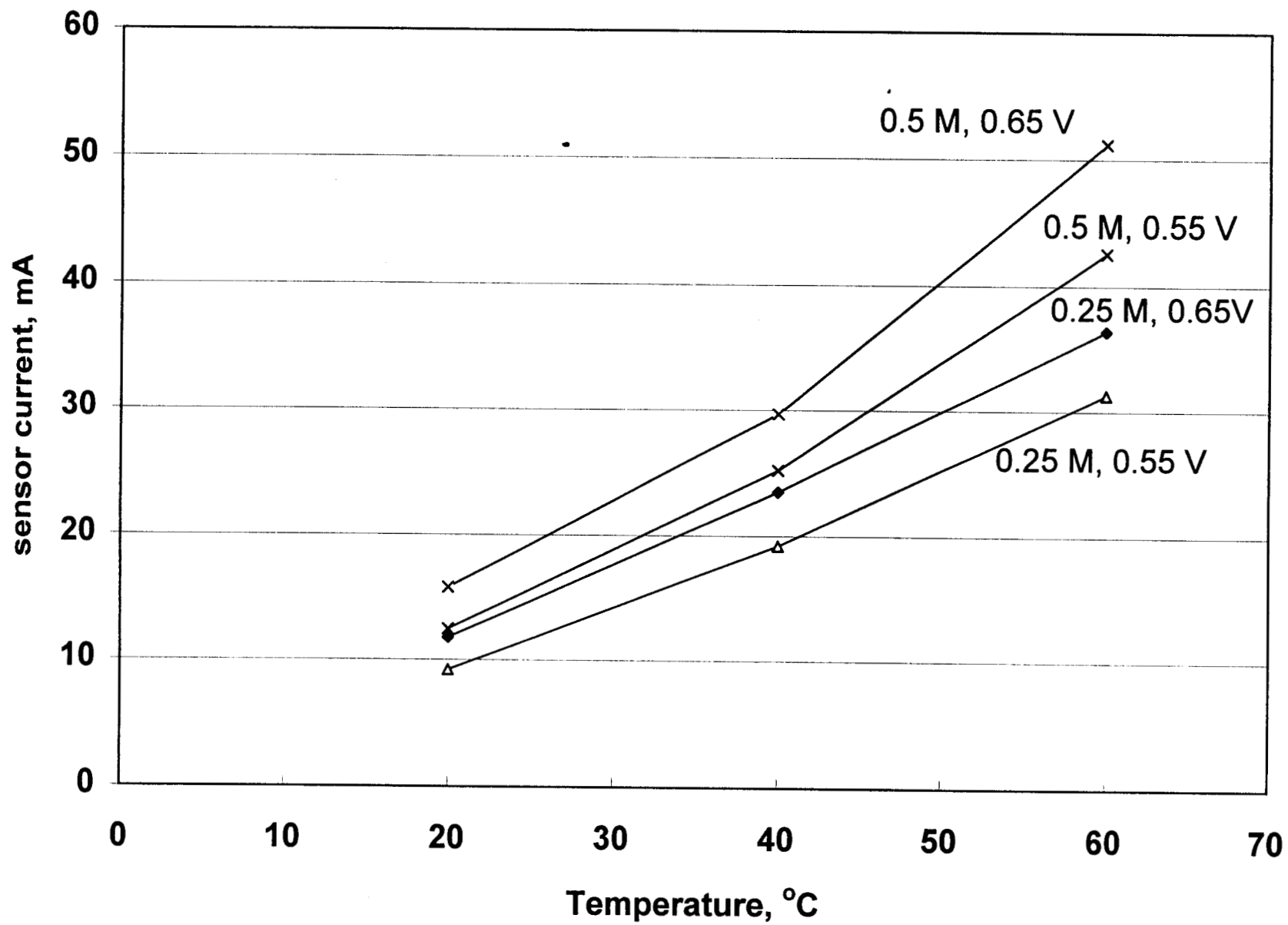


Fig. 3





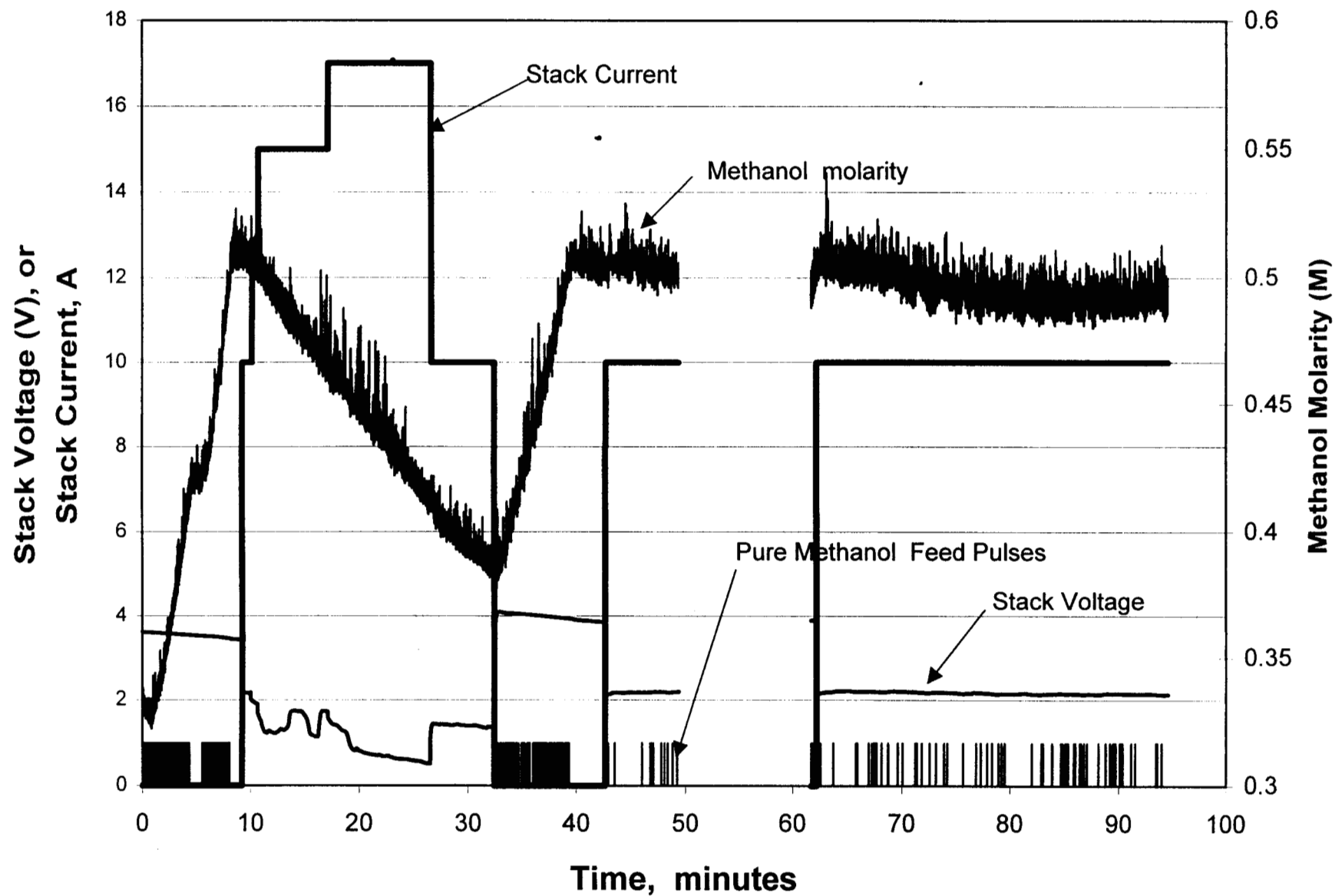


Fig. 6

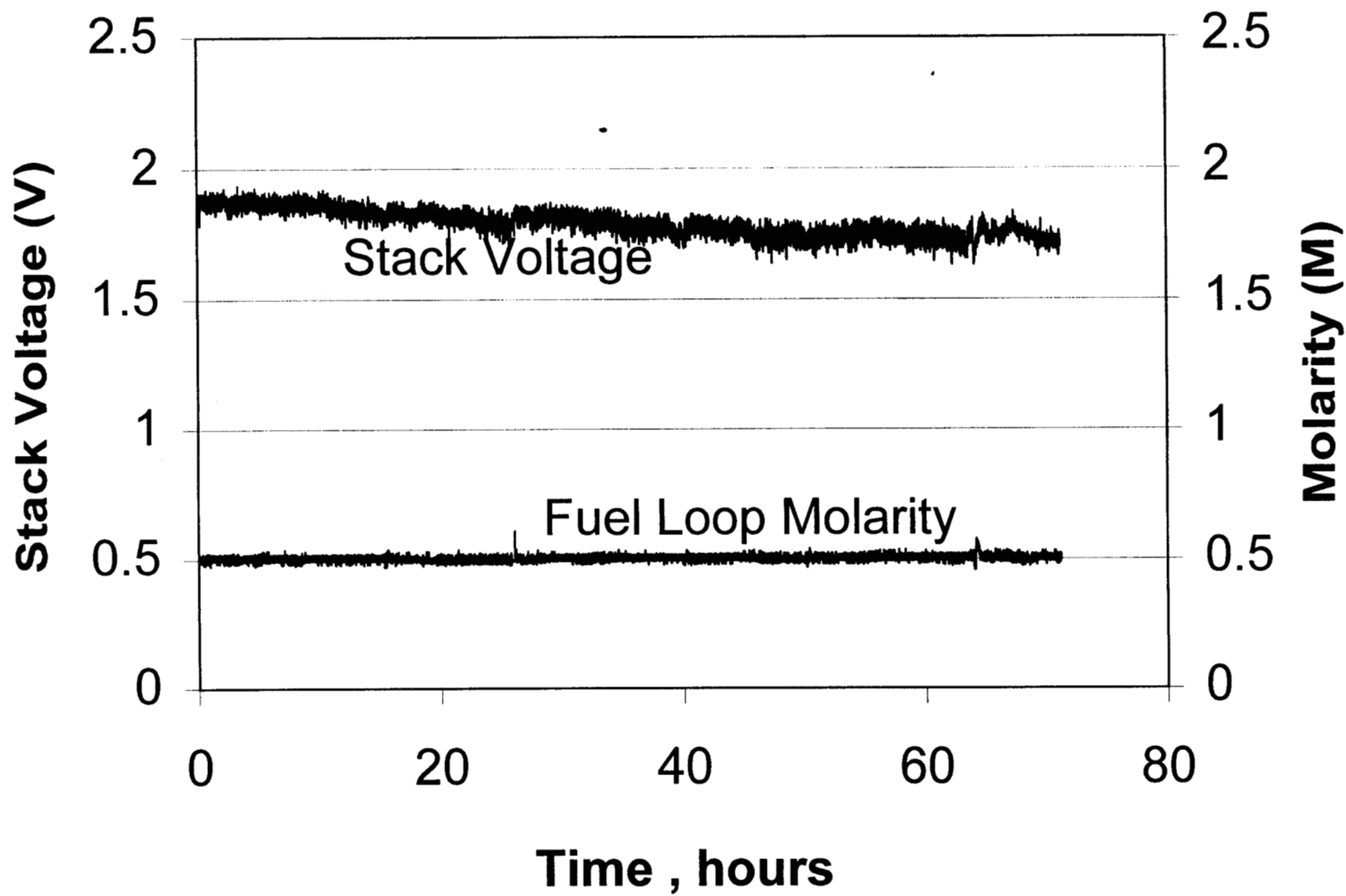


Fig. 7